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Published in:
Chemical Physics Letters

DOI:
10.1016/S0009-2614(97)01367-5

Publication date:
1998

20 February 1998

ELSEVIER

Chemical Physics Letters 284 (1998) 63–70

CHEMICAL PHYSICS LETTERS

Exchange narrowing in dynamically disordered molecular aggregates

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Received 21 August 1997

Abstract

We study the absorption lineshape for one-dimensional molecular aggregates with colored dynamic disorder. We show that exchange narrowing of the absorption spectrum, which is well-known in the limit of static disorder, also occurs for fast fluctuations, provided the fluctuation rate λ is not large compared to the intermolecular excitation transfer interaction J. For small aggregates, the narrowing factor is found to equal the number of molecules in the aggregate, while for large aggregates it saturates at $\sqrt{8J/\lambda}$ ($\lambda/J \ll 4$). These results are derived for dichotomic noise, but we argue that they also hold in the fast-fluctuation limit of other Markov processes. © 1998 Elsevier Science B.V.

1. Introduction

The dynamics of excitons in molecular assemblies, like J-aggregates [1] and biological light-harvesting systems [2], are strongly affected by the host medium. For example, the chromophores in quasi-one-dimensional J-aggregates embedded in low-temperature glasses suffer from strong static frequency disorder imposed by the structural disorder of the glass [3]. For aggregates in room temperature solutions, an even more complicated situation arises, as the environment may then not be considered static [4]. A well-known phenomenological way to model a dynamic environment (bath), is to assume that it imposes a classical stochastic fluctuation on the transition frequencies of the chromophores [5–7]. This level of modeling involves two frequency scales: the amplitude of the fluctuations (Δ) and their inverse correlation time (λ). Although this model is strictly speaking only valid for temperatures that are high compared to the frequency of the bath modes [7,8], it has been used very successfully to describe ultrafast spectroscopies, involving fast bath modes, for single molecules in solution [9]. In the fast fluctuation limit ($\Delta \ll \lambda$), the single-molecule absorption line undergoes motional narrowing: with growing λ, its width decreases according to Δ^2/λ due to the fact that for smaller correlation times each realization of the stochastic process averages more effectively over the evolution of the phase of the molecular transition dipole.

The case of an aggregate of interacting molecules, each of which undergoes stochastic fluctuations, is much more complicated, as it involves a third frequency scale: the intermolecular transfer interaction J. Only the white-noise limit ($\lambda \gg \Delta, J$) is exactly solvable and leads to the Haken-Strobl model with a homogeneous exciton dephasing rate $\Gamma = \Delta^2/\lambda$ [10,11]. For finite correlation times, one generally has to resort to approximate theories, like the dynam-

PII S0009-2614(97)01367-5

ical coherent potential approximation [12] or cumulant expansions [13,14].

In molecular aggregates, not only *motional* narrowing of fluctuations occurs, but also *exchange* narrowing [5,12,15]: due to the intermolecular excitation transfer, the excitation probes more realizations of the frequency fluctuations, and thus more effectively averages over them. This narrowing effect, which somewhat unfortunately is sometimes also referred to as motional narrowing [4,16,17], is well-known for J-aggregates with static disorder and is generally believed to cause the characteristic sharpness of the absorption band in these systems. In small aggregates of molecules with mutually *independent* static frequency disorder, narrowing occurs with a factor of the order $\sqrt{N}$ [15,16]. If the aggregate length exceeds the exciton delocalization length (N_{del}) imposed by the disorder, however, this factor is replaced by $\sqrt{N_{\mathrm{del}}}$ [3,15].

In this Letter, we focus on the opposite case: exchange narrowing of *fast* fluctuations. In particular, we investigate whether the motionally narrowed single-molecule line width of Δ^2/λ may be further narrowed by the intermolecular transfer interactions and, if so, how this extra narrowing depends on the aggregate size and the three frequency scales of the model. These questions were recently put forward by Van Burgel, Wiersma, and Duppen in their analysis of fs experiments on J-aggregates in solution [4].

The outline of this Letter is as follows: in Section 2, we describe the model and the method used to calculate the absorption spectrum for small aggregates. In Section 3, we present exact numerical results which demonstrate exchange narrowing and we derive an analytical expression for the exchange narrowing factor. A physical discussion of our results and a comparison to previous work are given in Section 4, while in Section 5 we conclude.

2. Model and method

We consider a one-dimensional aggregate that consists of N two-level molecules with nearest-neighbor excitation transfer interactions J. Modeling the effect of the environment by a stochastic modulation of the molecular transition frequencies, the Frenkel exciton Hamiltonian for this system reads ($\hbar = 1$),

$$\hat{H}(t) = \sum_{n=0}^{N-1} \Big[\big(\omega_0 + \Delta_n(t) \big) \hat{b}_n^{\dagger} \hat{b}_n + J\Big(\hat{b}_n^{\dagger} \hat{b}_{n-1} + \hat{b}_{n+1}^{\dagger} \hat{b}_n \Big) \Big] . \tag{1}$$

Here, $\hat{b}_n^{\dagger}$ and $\hat{b}_n$ denote the Pauli creation and annihilation operator [18], respectively, for an excitation on molecule n, ω_0 is the average molecular transition frequency, and $\Delta_n(t)$ is the modulation of the frequency of molecule n at time t. We impose periodic boundary conditions: $\hat{b}_N^{\dagger} = \hat{b}_0^{\dagger}$.

We will assume that the $\Delta_n(t)$ are independent dichotomic Markov processes [19,20] of amplitude Δ and correlation time λ^{-1}. Thus, at time t, each $\Delta_n(t)$ either has the value $+\Delta$ or $-\Delta$, while its correlation function decays according to:

$$\langle \Delta_m(t) \Delta_n(\tau) \rangle = \delta_{mn} \Delta^2 \, \mathrm{e}^{-\lambda |t-\tau|} . \tag{2}$$

For large λ, the fluctuation varies rapidly between $+\Delta$ and $-\Delta$, whereas for $\lambda = 0$ the model describes static dichotomic disorder. The case of finite λ is referred to as colored dichotomic noise.

The linear absorption spectrum of an aggregate is determined by the two-time correlation function of its total transition dipole $\Sigma_n \mu_n(\hat{b}_n^{\dagger} + \hat{b}_n)$, where μ_n is the transition dipole of molecule n. For simplicity, we will assume that all molecules have equal transition dipoles μ_z that are all oriented perpendicular to the plane of the ring formed by the aggregate. In the rotating wave approximation, the line shape is then given by [20]:

$$I(\omega) = \mu_z^2 \, \mathrm{Re} \sum_{n=0}^{N-1} \int_0^{\infty} \mathrm{d}t \, \mathrm{e}^{i\omega t} \langle X_n(t) \rangle , \tag{3}$$

Here, $\langle \ldots \rangle$ denotes averaging over the stochastic frequency modulations and the functions $X_n(t)$ are sums of one-exciton Green functions:

$$X_n(t) \equiv \sum_{m=0}^{N-1} \langle 0 | \hat{b}_n \hat{U}(t) \hat{b}_m^{\dagger} | 0 \rangle . \tag{4}$$

$\hat{U}(t)$ is the time evolution operator obeying $\mathrm{d}\hat{U}/\mathrm{d}t = -i\hat{H}(t)\hat{U}$ and $|0\rangle$ denotes the aggregate's ground state, where all molecules are in the ground state.

To calculate $\langle X_n(t) \rangle$, one derives its equation of motion $\mathrm{d}\langle X_n(t) \rangle / \mathrm{d}t$ [20,21]. This equation couples

$\langle X_n(t)\rangle$ to $\langle X_{n\pm1}(t)\rangle$ and $\langle X_n(t)\Delta_n(t)\rangle$. The latter variables couple to averages with one X and two fluctuations, etc. A hierarchy of equations of motion is thus derived. In contrast to, e.g., the Gauss–Markov stochastic process, the dichotomic fluctuations allow this hierarchy to close, because $\Delta_n^2(t) = \Delta^2$ for all n and all t. Thus, a closed set of $N2^N$ linear equations of motion may be derived, a fact recognized and used by Reineker, Barvík, and coworkers to numerically study effects of colored noise [20].

The size of this closed set of equations imposes strong restrictions on the aggregate size that can be treated. Thus far, only results for N up to 6 have been reported [20]. However, by exploiting the periodic boundary conditions and the fact that all molecules are *on average* identical, the size of the set can be reduced by a factor of N. For example, $\langle X_n(t)\rangle = \langle X_0(t)\rangle$ and in Eq. (3) $\sum_{n=0}^{N-1}\langle X_n(t)\rangle$ may simply be replaced by $N\langle X_0(t)\rangle$. Using similar symmetries of the higher-order variables in the hierarchy, the following set of 2^N variables gives a closed hierarchy:

$$X^{(0)}(t) \equiv \langle X_0(t)\rangle, \tag{5}$$

$$X^{(m)}(n_1,n_2,\ldots,n_m;t) \equiv \langle X_0(t)\,\Delta_{n_1}(t)\,\Delta_{n_2}(t)\ldots\Delta_{n_m}(t)\rangle/\Delta^m, \tag{6}$$

where $1 \le m \le N$ and $0 \le n_1 < n_2 < \ldots < n_m \le N-1$.

Using the time evolution of $\hat{U}$ and the properties of correlation functions of dichotomic processes [21], the general equation of motion that governs this hierarchy reads:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}X^{(m)}(n_1,n_2,\ldots,n_m;t) &= -(i\omega_0 + m\lambda)X^{(m)}(n_1,n_2,\ldots,n_m;t)\\ &\quad - iJX^{(m)}(n_1-1,n_2-1,\ldots,n_m-1;t)\\ &\quad - iJX^{(m)}(n_1+1,n_2+1,\ldots,n_m+1;t)\\ &\quad - i\Delta(1-\delta_{n_1,0})X^{(m+1)}(0,n_1,n_2,\ldots,n_m;t)\\ &\quad - i\Delta\delta_{n_1,0}X^{(m-1)}(n_2,\ldots,n_m;t).\end{aligned} \tag{7}$$

The set of variables $X^{(m)}$ defined above form a vector $\boldsymbol{X}$ of dimension 2^N. As first element of this vector, we use $X^{(0)}$. The equation of motion for $\boldsymbol{X}$ now reads

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{X}(t) = -i\boldsymbol{R}\boldsymbol{X}(t), \tag{8}$$

where the matrix $\boldsymbol{R}$ follows from Eq. (7). The initial condition is $[\boldsymbol{X}(t=0)]_1 = X^{(0)}(t=0) = 1$ and all other components of $\boldsymbol{X}$ vanish at $t=0$. By Laplace transforming this equation and using Eq. (3), one arrives at

$$I(\omega) = -N\mu_z^2\,\mathrm{Im}\{\omega\mathbf{1} - \boldsymbol{R}\}^{-1}_{1,1}, \tag{9}$$

with the last factor denoting the (1,1) element of the inverse of the matrix $\omega\mathbf{1} - \boldsymbol{R}$. We stress that this result is exact. Of course, for any reasonable value of N, the actual evaluation has to be numerical.

3. Results

Before considering the absorption spectrum for aggregates, we briefly discuss the case $N = 1$, i.e., an ensemble of monomers. This can be solved exactly [19]. For $\Delta \gg \lambda$, we are in the static limit, where each molecule has a random static frequency which either is $\omega_0 + \Delta$ or $\omega_0 - \Delta$. This gives an absorption spectrum with two narrow spikes. For decreasing Δ/λ, both lines broaden, until they merge into one peak for $\Delta/\lambda \approx 1$. Upon further decreasing Δ/λ this peak narrows according to Δ^2/λ (HWHM), which is the motional narrowing effect described in the Introduction. Motional narrowing is a single-molecule property and occurs for any Markov process (not only the dichotomic one) that has a second moment [22].

For $N > 1$, we numerically calculated the absorption spectra using the method outlined in the previous section. We considered aggregates of up to $N = 9$ molecules and used various values of Δ/J and λ/J. In the static limit ($\Delta \gg \lambda$), the spectra contain a collection of narrow peaks in the frequency interval $[\omega_0 + 2J - \Delta, \omega_0 + 2J + \Delta]$, resulting from all possible eigenstates on random aggregates with

two types of molecules (frequency $\omega_0 \pm \Delta$). For growing N the peaks become denser; for growing Δ/J, more peaks become prominent. Keeping Δ/J fixed and increasing λ/J, leads to the merging of all discrete peaks into one broader feature, which then motionally narrows for $\lambda > \Delta$. These features are basically the same as observed for $N \leq 6$ [20]. In this Letter, we focus completely on the N dependence of the single peak that shows up in the motional narrowing regime.

Figs. 1(a)–(c) give the motionally narrowed absorption spectra for $N = 3$, 6, and 9, with λ increasing from $0.25J$ to $16J$ (from the higher to the lower peaks), *while keeping* $\Delta^2/\lambda = 0.5J$ fixed. The area under each of the peaks is independent of Δ, λ, and J and is given by $\pi N \mu_z^2$. From these figures it is observed that if λ is large, all peaks get, independent of the aggregate size, the same width of $0.5J$, which agrees with the single-molecule motional narrowing width of Δ^2/λ. For decreasing λ/J, however, it is also seen that the peak width can get considerably smaller than this monomer value and that this extra narrowing is more prominent if N is increased. The latter is very clear from Fig. 1(d), which gives the spectra per molecule for the three considered ring sizes at $\Delta = \lambda = 0.5J$. These observations imply that indeed *exchange narrowing* of fast fluctuations occurs.

Further quantitative insight into the line shape and the exchange narrowing can be obtained by analytical analysis. To this end, we truncate the hierarchy of 2^N equations of motion, by neglecting the variables $X^{(2)}$ relative to the $X^{(1)}$. This is equivalent to the random phase approximation (RPA) type factorization, $\langle X_0(t)\Delta_n(t)\Delta_m(t)\rangle = \langle X_0(t)\rangle\langle \Delta_n(t)\Delta_m(t)\rangle$, which was proposed in Refs. [20,23] and shown to be a good approximation for dimers and trimers ($N = 2,3$), as long as $\Delta < \sqrt{2}\,\lambda$, i.e., in the motional narrowing regime.

After this truncation, the matrix $\boldsymbol{R}$ can be reduced

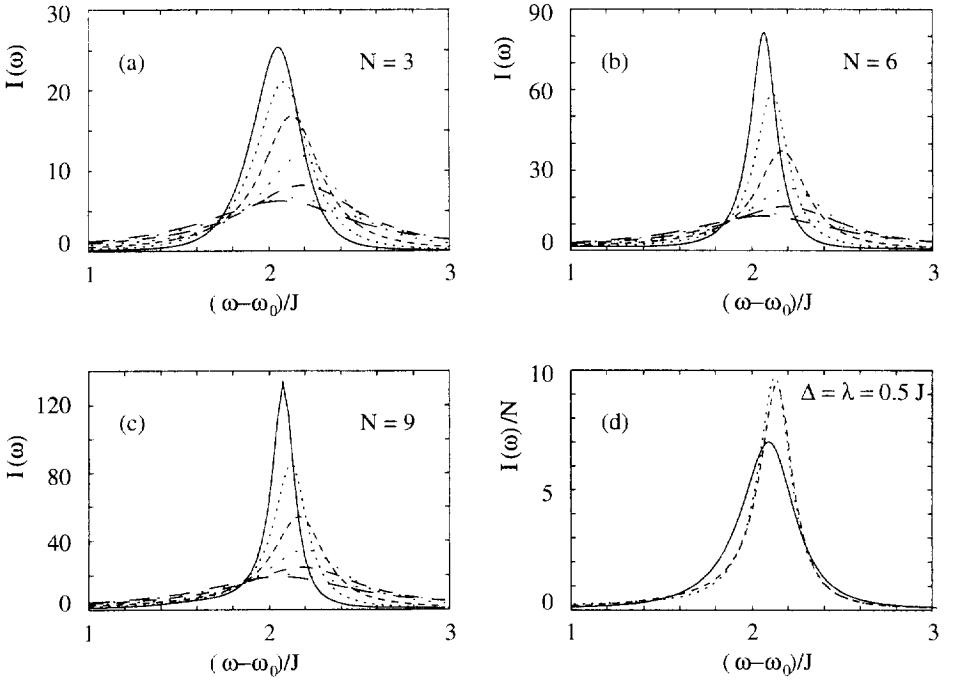

Fig. 1. (a)–(c) Absorption spectra for ring aggregates of $N = 3$,6, and 9 molecules. For each N, λ/J takes the values 0.25, 0.5, 1, 2, 4, 8, and 16, when going from the highest to the lowest peak. The ratio $\Delta^2/\lambda = 0.5J$ is kept constant for all spectra. Panel (d) compares the spectra for the three ring sizes at $\Delta = \lambda = 0.5J$ (solid line: $N = 3$, short dash: $N = 6$, and long dash: $N = 9$). $I(\omega)$ is given in units of μ_z^2/J.

to a matrix $\boldsymbol{R}'$ of dimension $N+1$ in the subspace of $X^{(0)}$ and $X^{(1)}(n)$ $(n=0,\ldots,N-1)$:

$$\boldsymbol{R}' = \begin{pmatrix} \omega_0 + 2J & \boldsymbol{A} \\ \boldsymbol{A}^{\mathrm{T}} & \boldsymbol{B} \end{pmatrix}. \tag{10}$$

Here, $\boldsymbol{A}$ is the N-dimensional vector $(-\Delta,0,\ldots,0)$, while $\boldsymbol{B}$ is the $N\times N$ matrix that has $\omega_0 - i\lambda$ as its diagonal elements, J on its two subdiagonals, and J as its upper right hand and lower left hand elements. The matrix $\boldsymbol{B}$ is equivalent to the Hamiltonian for a homogeneous ring of N molecules with nearest-neighbor interaction J and effective transition frequency $\omega_0 - i\lambda$. As the latter problem is easily diagonalized, it is straightforward to solve for the (1,1) element of $(\omega - \boldsymbol{R}')^{-1}$, leading to the line shape:

$$I(\omega) = -N\mu_z^2 \,\mathrm{Im}\left\{ \frac{1}{\omega - \omega_0 - 2J - \Sigma(\omega)} \right\}, \tag{11}$$

with

$$\Sigma(\omega) = \frac{\Delta^2}{N\lambda} \sum_{k=0}^{N-1} \frac{\lambda}{\omega - \omega_0 - 2J\cos\left(\dfrac{2\pi k}{N}\right) + i\lambda}, \tag{12}$$

the complex and frequency dependent exciton self-energy.

For $N \le 9$, $I(\omega)$ given by Eq. (11) indeed turns out to be in excellent agreement with our exact numerical spectra as long as $\lambda > \Delta$. This confirms that in the motional narrowing regime the RPA is valid. Of course, Eq. (11) is much easier to evaluate (for arbitrarily large N) and we therefore used it to further study the width W (HWHM) of the absorption peak in the motional narrowing regime. We may, in fact, go one step further and make a pole approximation in Eq. (11) by replacing $\Sigma(\omega)$ by $\Sigma(\omega_0 + 2J)$. We have checked that this approximation is good for arbitrary N, as long as $\Delta < \lambda/2$. The thus obtained line shape is Lorentzian, is centered at $\omega_0 + 2J + \mathrm{Re}\,\Sigma(\omega_0 + 2J)$, and has width (HWHM) $W = -\mathrm{Im}\,\Sigma(\omega_0 + 2J)$. From Eq. (12), one finds that

$$W = \frac{1}{F_e}\frac{\Delta^2}{\lambda}, \tag{13}$$

with

$$F_e = N\left[\sum_{k=0}^{N-1} \frac{\lambda^2}{4J^2\{1-\cos(2\pi k/N)\}^2 + \lambda^2} \right]^{-1}. \tag{14}$$

F_e is the exchange narrowing factor by which the single-molecule line width in the motional narrowing regime is further reduced due to the intermolecular interactions. Note that F_e does not depend on Δ. A plot of F_e as a function of N and λ/J is given in Fig. 2.

Straightforward analysis of Eq. (14) shows that $1 \le F_e \le N$. For $\lambda/J \gg 1$, $F_e = 1$, which agrees with the Haken-Strobl result (see Introduction) [10,11]. For $\lambda/J \ll 1$ and $(N/2\pi)^4 \ll (J/\lambda)^2$, Eq. (14) gives $F_e = N$. Above a certain aggregate size, however, this N-scaling saturates and the absorption spectrum per molecule no longer depends on N. These features are clearly seen in Fig. 2 and indeed capture very well the salient details of the exact spectra in Fig. 1(d), where it may be observed that the narrowing for $N=3$ occurs with a factor of approximately 3, while the spectrum for $N=9$ already closely resembles the one for $N=6$. The saturated value of the narrowing factor is easily calculated from Eq. (13) by taking $N\to\infty$ and replacing the sum over k by an integral over $\kappa = 2\pi k/N$. This leads to the exchange narrowing factor for the infinitely long aggregate:

$$F_e^{\infty} = \sqrt{\frac{2\lambda^2 + 32J^2}{\lambda^2 + \lambda\sqrt{\lambda^2 + 16J^2}}}. \tag{15}$$

It follows that for $\lambda/J \gg 4$, F_e^{∞} tends to unity, while

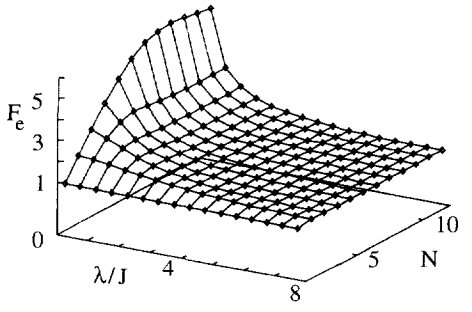

Fig. 2. The exchange narrowing factor Eq. (14) as a function of λ/J and N.

for $\lambda/J \ll 4$, $F_c^{\infty} = \sqrt{8J/\lambda}$. F_c^{∞} may also be viewed as the aggregate size at which the saturation of the spectral lineshape sets in.

To end this section, we note that within the above truncation approximation our results are not limited to the dichotomic process. Any other stochastic process with two-time correlator Eq. (2), in particular a Gauss–Markov one, would yield identical RPA results.

4. Discussion

We now turn to the physical explanation of our observations. First consider the case of vanishing disorder ($\Delta = 0$). We then simply have exciton states that are coherently delocalized over the entire ring. Only one of these states is observable in absorption: the $k = 0$ Bloch state, $\sum_n \hat{b}_n^{\dagger}|0\rangle/\sqrt{N}$, with frequency $\omega_0 + 2J$. Next, consider finite fluctuations that are slow on the time scale of excitation transfer ($\lambda/J \ll 1$), while N is not too large. Then, we may still consider exciton states, which adiabatically follow the molecular fluctuations. As we are most interested in the motional narrowing regime ($\Delta < \lambda$), we may also assume that Δ/J is small enough so that the adiabatic exciton states are still completely delocalized over the ring. We may then use perturbation theory to calculate the effect of the molecular fluctuations on the exciton states. To first order in Δ, the frequency fluctuation of the $k = 0$ state around the value $\omega_0 + 2J$ reads:

$$\Delta_{k=0}(t) = \sum_n \Delta_n(t)/N, \tag{16}$$

which simply is the average of the molecular fluctuations. Using Eq. (2), $\Delta_{k=0}(t)$ is found to have a correlator

$$\langle \Delta_{k=0}(t)\,\Delta_{k=0}(\tau)\rangle = \Delta_N^2\, e^{-\lambda|t-\tau|}, \tag{17}$$

with $\Delta_N = \Delta/\sqrt{N}$. Thus, the amplitude of the fluctuation is reduced by a factor $\sqrt{N}$ compared to the single molecule, while its time scale is not affected ($\lambda_N = \lambda$).

Exactly the same results would be obtained for the more frequently considered Gauss–Markov fluctuations. In the static limit, this gives the familiar explanation of exchange narrowing by the factor $\sqrt{N}$ [15,16]. The difference between both types of fluctuations is that for Gaussian molecular fluctuations, $\Delta_{k=0}(t)$ according to Eq. (16) is still a Gaussian process, while in the case of dichotomic noise $\Delta_{k=0}(t)$ is not dichotomic. In the motional narrowing regime, however, only the second moment of the process $\Delta_{k=0}(t)$ is important; other details of its character only show up in the far wings of the line shape. In fact, the width of the absorption line associated with the fluctuating $k = 0$ exciton level is then given by $\Delta_N^2/\lambda = \Delta^2/(N\lambda)$, which is smaller than the monomer line width by a factor of N. This agrees with what we found in the previous section for $(\lambda/J)^2 \ll (2\pi/N)^4$.

If λ/J or N increase, the adiabatic approximation breaks down and we should strictly speaking resort to a density matrix approach. In stead of following that route, however, we will estimate the line width by introducing effective adiabatic exciton states on finite intervals of the aggregate. Let us define a domain of N_c molecules on the ring such that the time scale N_c/J of excitation transfer over this domain equals the time scale $(N_c\lambda)^{-1}$ during which one fluctuation occurs on one of the N_c molecules. Thus, N_c gives the typical domain size for which the adiabatic approximation starts to break down. Equating the two time scales, we arrive at $N_c = \sqrt{J/\lambda}$. If $N_c > N$, we return to the above situation: narrowing of fast fluctuations occurs with a factor N. If $1 < N_c < N$, the narrowing factor is $F_c = N_c$, i.e., the ring size no longer limits the line shape. In particular, for an infinitely long aggregate and $J > \lambda$, we arrive at $F_c \sim \sqrt{J/\lambda}$, which agrees with the limiting behavior that we found in Section 3. Finally, if $N_c < 1$ (i.e., $J < \lambda$), the identification of N_c with a chain interval can no longer be made. In this case, no intermolecular excitation transfer occurs before a fluctuation takes place, so that exchange narrowing is impossible ($F_c = 1$). This is the white-noise limit, in which the excitation already efficiently averages over all possible phase evolutions before transfer to another molecule can help to decorrelate the frequency. In the current line of reasoning, we tacitly assumed that the amplitude Δ of the fluctuations does not limit the delocalization of the adiabatic excitons to a size smaller than N_c. In the fast fluctuation limit ($\lambda > \Delta$), which we are focussing on, this is indeed the case, as the delocalization length scales like $(J/\Delta)^{2/3}$ [3,24].

To conclude this section, we make a brief comparison to previous studies of the line width of dynamically disordered molecular systems. In particular, we consider the works of Sumi [12] and Blumen and Silbey [13]. Using the dynamical coherent potential approximation [12] and cumulant expansions [13,14], these authors considered Gauss–Markov fluctuations in three-dimensional crystals of infinite size. They did not study size scaling. If the oscillator strength is concentrated at one of the band edges (as is the case for our model), both studies yield a line width $W = \alpha\Delta^2/(B^2+\lambda^2)^{1/2}$ for $\Delta \ll (B^2+\lambda^2)^{1/2}$ and $\lambda \neq 0$. Here $2B$ is the exciton band width ($4J$ for our system) and α is a constant that slowly depends on B/λ for $0 < B/\lambda < 100$. This behavior is in marked contrast to the line width $W = \Delta^2/(8J\lambda)^{1/2}$ which we find for infinite chains in the case $4J \gg \lambda > \Delta$. This difference is due to the dimensionality: if we apply the cumulant expansion of Ref.[13] to a ring aggregate with Gaussian noise, we recover our RPA result within the pole approximation, i.e., Eqs. (13) and (14). This, again, demonstrates that in the fast-fluctuation regime only the second moment of the fluctuation process affects the line shape.

5. Concluding remarks

In this Letter, we have studied the absorption line shape of ring aggregates of which the molecules undergo independent dichotomic frequency fluctuations. We have found that for fast fluctuations ($\lambda > \Delta$) the absorption line width exhibits both motional narrowing and exchange narrowing. Motional narrowing is a single-molecule property, whereas exchange narrowing is a collective effect. We have shown that the dependence of the exchange narrowing factor on the various system parameters (Δ/J, λ/J, and N) can physically be understood by introducing the notion of adiabatic exciton states on finite intervals of the aggregate. This explanation shows that the amplitude of the fluctuations on the exciton level is reduced due to the excitation transfer, while the time scale is not affected.

It may seem rather restrictive that for exchange narrowing of fast fluctuations to occur, the fluctuations should not be fast compared to the excitation transfer. We note, however, that even for $\lambda = J$ appreciable exchange narrowing occurs ($F_e^\infty = 2.6$). This ratio of parameters is not unrealistic: typical values for J in J-aggregates are $10^3\,\mathrm{cm}^{-1}$ [3,4], while fast fluctuation rates for monomers in solution may be of the same order [9].

The limiting value F_c^∞ given by Eq. (15) gives the chain size at which the absorption spectrum starts to saturate. It is tempting to identify F_e^∞ with an exciton coherence length, but this is incorrect. For example, in the white-noise limit, when our model reduces to the Haken-Strobl model, we find $F_c^\infty = 1$, while it is well-known that coherent transport of the excitation over many molecules is still possible in this limit, provided that $\Gamma = \Delta^2/\lambda \ll J$ [11].

We finally note that the effect of exchange narrowing of fast fluctuations is not limited to our special model. As indicated in Sections 3 and 4 already, for other Markov processes (such as Gaussian fluctuations) exchange narrowing for $\Delta < \lambda$ occurs with exactly the same factor as for dichotomic noise. Second, the effect does not rely on the periodic boundary conditions. For open boundary conditions more complicated expressions are obtained, which for $N \to \infty$ reduce to the ones we found for the ring [25]. Finally, also the restriction to transition dipoles pointing perpendicular to the plane of the ring is not crucial. The analysis for dipoles that lie in the plane, which is of interest to exciton dynamics in light-harvesting systems, will be published elsewhere [25].

Acknowledgements

It is a pleasure to thank Dr. K. Duppen for stimulating discussions.

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